Epitaxial Si films on Ge(100) grown via H/Cl exchange

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(Received 13 August 1992; accepted for publication 25 November 1992)

Thin Si films have been grown isothermally on Ge(100) substrates using alternating exposures of Si_2H_6 and Si_2Cl_6, maintaining chlorine and hydrogen surface termination. At 465 °C, film growth rate is roughly 2 monolayer per cycle (one cycle equals 1 Si_2H_6 and 1 Si_2Cl_6 exposure). At 475 °C a uniform epitaxial film is obtained, while islanding is observed at higher T. This process is thermally activated and is not strictly self-limiting, but has certain desirable characteristics of atomic layer epitaxy growth.

The primary advantage seen in growth of Si and SiGe alloys via the layer-by-layer growth method known as atomic layer epitaxy (ALE)[1,2] is fine control over deposited layer thickness. Approaches to ALE of Si have included pulsed laser heating,[3] synchrotron radiation,[4] or high temperature (T)[5] to regenerate a bare, dangling bond (db) terminated, Si surface following saturation exposure to Si_2H_6[3] or $SiCl_2H_2$.[4,5] We report here on the first low temperature, isothermal, growth of thin epitaxial Si films using hydrogen/chlorine exchange chemistry, specifically alternating exposures of Si_2Cl_6 and Si_2H_6. Rather than regenerate a db-terminated surface, this method maintains surface termination with a mixed Cl+H adlayer. The adlayer acts as a surfactant,[6] resulting in continuous, highly uniform, Si films grown below 500 °C. This process is not strictly self-limiting, but resembles ALE in that precise control over Si layer thickness is obtained.

Here, each growth cycle consists of separate exposure to Si_2H_6 and Si_2Cl_6. An initial Si_2H_6 exposure largely covers the Ge(100) surface with Si. Thereafter, Si_2Cl_6 is dosed onto the H-terminated surface (30 s at 0.002 Torr), and Si_2H_6 is dosed onto the Cl-terminated surface (300 s at 0.005 Torr). Using surface sensitive direct recoiling (DR) analysis, the exposures of Si_2H_6 and Si_2Cl_6 required to complete the exchange reactions have been reported as a function of T on Si(100),[7] but film crystallinity and morphology were not studied. At 515 °C and below, the chlorination step is self-limiting. The Cl removal step using Si_2H_6 appears to be kinetically controlled[7] and is not self-limiting. We designate these films as Si*. We show here that the Si* thickness is a linear function of the number of growth cycles, and the growth rate is $\simeq 2$ monolayer (ML)/cycle at 465 °C. 1 ML equals 6.8×10^{14} Si atoms cm^{-2}.

The Si on Ge epitaxy system has remained relatively unexplored compared to Ge on Si. Heteroepitaxy has been investigated for Si on Ge(100) using electron spectroscopies[8] and Si on Ge(111) using medium energy ion scattering (MEIS).[9] In the absence of surfactants, the normal growth mode is island formation (Volmer–Weber).[8,9] Copel and co-workers have utilized As as a surfactant in the growth of Si on a thin Ge layer on Si(100), which changes the growth mode to uniform, layer by layer growth (Frank–Van der Merwe).[6] Here, we report a dramatic effect of growth T on the Si* morphology in the range 465–515 °C. Below 500 °C, the surface remains terminated with Cl and/or H during growth, and this adlayer acts as a surfactant[6] giving uniform Si growth. This Cl+H adlayer may also inhibit Ge out-diffusion through the Si* film.

Thin Si films were grown isothermally in a (cold wall) stainless-steel chamber (base pressure 2×10^{-9} Torr) equipped with low energy diffraction (LEED) optics. The Ge(100) substrates were cleaned by 5 cycles of Ar^+ sputtering (5–10 min) and flashing to 750 °C, followed by annealing at this T for 5 min. Good (2×1) LEED patterns were observed, and analysis by DR in a separate chamber showed the Ge(100) to be atomically clean after this procedure. *Ex situ* studies with cross-sectional transmission electron microscopy (XTEM) and MEIS were performed with a native oxide on the Si* films. Residual Cl in the films was <0.1 at. % as measured by secondary ion mass spectrometry.

Film morphology was studied by XTEM, with Si* grown for 20 growth cycles at 3 temperatures: 465, 475, and 515 °C. Figure 1 shows XTEM micrographs from the 515 °C (top) and 475 °C (bottom) films. Common to both pictures are the (111) lattice fringes which propagate from the Ge(100) substrate into the Si*, confirming that the Si* is epitaxial. At 515 °C, the film is characterized by few defects. However, the film is also highly nonuniform in thickness, consisting of large islands, apparently joined by a thin Si layer visible at the sides of the micrograph. Selected area diffraction from the Si islands further confirmed the epitaxial quality of the Si*. At 475 °C, the Si film is continuous, very uniform in thickness (130 ± 10 Å), and contains an abundance of defects. Ge has a 4% larger lattice constant than Si, and the defects (dislocations and stacking faults) form in order to relieve strain in the Si* film. Homoepitaxy studies on Si(100) are in progress aimed at establishing the defect density intrinsic to this process. A film grown at 465 °C (XTEM not shown) exhibited uniform Si* thickness.

Information on Si* crystallinity, thickness, and interdiffusion with Ge was obtained from MEIS using a 200 keV He^+ beam. MEIS spectra for three samples grown at 465 °C appear in Fig. 2, with a solid line for the random incidence ($\times1$) and shaded spectrum for the aligned

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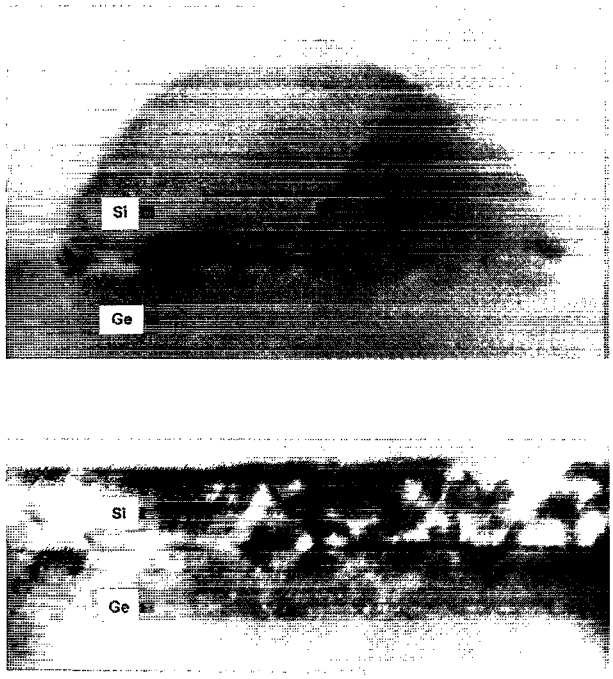

FIG. 1. Cross-section TEM micrographs of Si* films on Ge(100), both taken at 550 000 magnification. The spacing of (111) planes is 3.27 Å for the Ge substrate. In each panel, the diagonal lines are lattice images of (111) planes. Top panel: 20 cycles at 515 °C. The Si island is ≃250 Å thick at the center. Bottom panel: 20 cycles at 475 °C. The Si film is ≃130 Å thick.

(×5) geometries, respectively. The arrows at 191.6 keV indicate the energy for He^+ backscattering from a Ge surface layer. Such a layer might form by Ge out-diffusion to the Si* surface. Out-diffusion of Ge is negligible, giving <1 at. % Ge in the Si*, a result we confirmed by x-ray photoelectron spectroscopy. In the aligned spectra, all three of

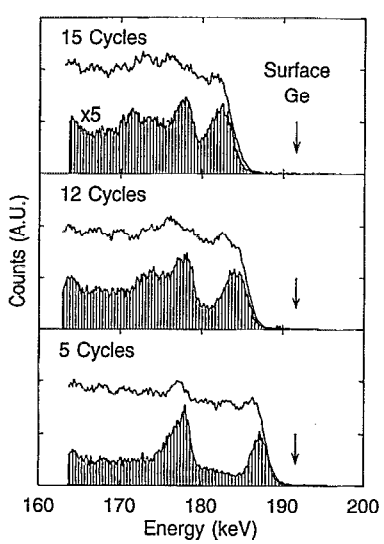

FIG. 2. MEIS spectra from Si* films on Ge(100) grown for the indicated number of cycles at 465 °C, using 200 keV He^+ ions. The He^+ beam is incident along a $(\bar{1}11)$ direction at 54.7° from the Ge(100) surface normal, and the detector is located at a 52.3° scattering angle. Solid line: random incident geometry, ×1. Shaded spectrum: aligned geometry, ×5.

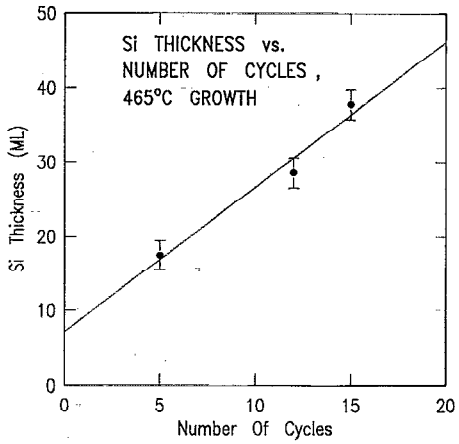

FIG. 3. Solid points: thickness of Si* film (derived from the MEIS data of Fig. 2) plotted vs number of growth cycles. Solid line: least-squares fit.

the films exhibit a Ge interface peak (187–183 keV) and a Si surface peak at ≃178 keV. A Si interface peak develops in the thicker films (170–175 keV). Scattering intensity from within the Si* film in the aligned geometry is roughly 10% of that for the random incidence geometry, consistent with the presence of strain relief defects seen in Fig. 1. (The aligned intensity is ≃2% for a high quality Si single crystal.)

Ions scattered from the Ge(100) interface lose energy during transit through the Si* overlayer, causing the Ge leading edge to shift below 191.6 keV in Fig. 2. The shift was converted to thickness of Si* using tabulated values of the stopping power. The result, plotted in Fig. 3, indicates that the Si* thickness correlates linearly to the number of growth cycles. This is a useful feature of the H/Cl exchange growth method. Independent evaluation by XTEM of the 15 cycle thickness agreed with the MEIS measurement within 2%. The solid line is a least squares fit to the data (slope=1.95 ML/cycle, y-intercept=7.2 ML). The nonzero y-intercept is considered below.

Elsewhere, we have speculated on the growth mechanism using Si_2H_6 and Si_2Cl_6 on the Si(100) surface.[7] *After* a continuous Si film is established on the Ge(100) surface, we speculate that ≃1/3 ML of Si* is grown with each self-limiting Si_2Cl_6 exposure (1 ML of Cl as monochloride gives 2/6 ML of Si). During the Si_2H_6 exposure (300 s), Si* is probably grown via the desorption of *both* H_2 and HCl. The amount of Si* grown from Si_2H_6 is expected to be T dependent, and is ≃1.6 ML at 465 °C.

We attribute the nonzero intercept in Fig. 3 to fast initial growth of Si* during the first Si_2H_6 exposure, caused by the rapid desorption of H_2 from the Ge(100) surface. Si growth from Si_2H_6 on Si(100) is rate limited by H_2 desorption below ≃550 °C.[10,11] The 1st order desorption rate for H_2 from Si(100) at 465 °C is $\simeq 10^{-2}$ s^{-1}.[12] On Ge(100), this rate is 10^4–10^5 faster.[13] Therefore, initial growth of Si* on Ge(100) should be significantly faster than similar growth on Si(100). Using DR analysis, we see nearly complete attenuation of the Ge DR signal after one growth cycle at 465 °C.[14]

Here we report the first low T, isothermal, growth of

epitaxial Si films using H/Cl exchange chemistry. Alternating exposures of Si_2H_6 and Si_2Cl_6 result in heteroepitaxy of Si on Ge(100) with a film thickness proportional to the number of growth cycles. Films grown below 500 °C are continuous and very homogeneous in thickness, but contain many strain relief defects.

The authors thank J. Cotte for SIMS analysis. This work is supported by the Office of Naval Research under Contract No. N00014-91-C-0080.

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